UV/Tio_2 photocatalytic reactor for real textile wastewaters treatment

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ABSTRACT

Textile dye wastewaters are characterized by strong colour, salts and other additives, high pH, temperature, chemical oxygen demand (COD) and biodegradable materials. Being aesthetically and environmentally unacceptable, these wastewaters need to be treated before their discharge. Anaerobic bioprocesses have been proposed as being environmentally friendly and relatively cheap; however, when applied to real effluent with a complex composition, they can fail. In this study, a photoreactor combining UV light and TiO_2, immobilized in cellulosic fabric, was applied for the treatment of two industrial textile wastewaters. High colour and COD removal, and detoxification, were achieved for both wastewaters, at controlled pH of 5.5. Effluents showed very poor biodegradability due to their complex composition; thus, the proposed process is an efficient alternative.

Key words | immobilized TiO_2, reactive dyes, textile wastewaters, UV/TiO_2 photocatalysis, wastewater additives

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INTRODUCTION

Incomplete exhaustion of dyes onto textile fibre during dyeing processes results in highly coloured effluents, even when dyes are at lower concentrations. The carcinogenic and teratogenic character of dyes themselves and of aromatic amines resulting from anaerobic reduction is also of concern (Pinheiro *et al.* 2004). Consequently, textile industries seek innovative and sustainable processes to treat end-of-line effluents, ensuring conformity with discharge limit tax values, as well as to minimize negative impacts on the surrounding environment and even to reuse water.

Difficult dye degradation is, in part, caused by the properties of the dyes, which are designed to resist light and constant washes. Conventional processes such as membrane filtration (Fersi & Dhahbi 2008), coagulation and flocculation (Solmaz *et al.* 2006), precipitation (Solmaz *et al.* 2007) and adsorption (Khan *et al.* 2004), mostly transfer the pollutants to another phase instead of removing them; in addition, those processes can be costly and can even add new chemicals to the treated medium (Pearce *et al.* 2003). Biological treatment systems to remove dyes effectively from large volumes of wastewater at low cost, including biosorption and biodegradation under aerobic, anaerobic or combined aerobic/anaerobic conditions with bacteria, fungi, plants, yeasts, algae and enzymes (McMullan *et al.* 2001; Mohan *et al.* 2005; Van der Zee & Villaverde 2005) have been proposed. Notwithstanding, most of the studies are focused on single dye or model baths, prepared at the best conditions for the microorganisms and enzymes. When applied to the real effluents with a complex composition, they can fail due to the inhibitory/toxic effects on non-adapted biomass caused by the presence of the diverse and high concentration wastewaters constituents.

Photocatalytic processes have been proposed as either a pre-treatment of wastewaters, applied until biodegradability is reached (Lapertot *et al.* 2006), or as a post-treatment (Basha *et al.* 2011). Photocatalytic systems by irradiation of TiO_2 particles are competent for wastewater treatment, because complete mineralization of most organic compounds with operation at mild conditions is achieved without producing sludge or harmful by-products (Huang *et al.* 2006). The TiO_2 catalyst is low cost, has a high surface area (7–50 $m^2\ g^{-1}$), is non-toxic, is chemically stable in aqueous media in a large pH range, is photostable and is able to utilize sunlight and air to produce many reactive species,

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including the powerful and non-selective oxidant hydroxyl radicals (HO•), to destroy organic compounds and turn them into harmless species such as CO_2, H_2O (Adams *et al.* 2006; Su *et al.* 2009). However, separation of TiO_2 powder from the liquid state and recycling catalyst can be challenging. Furthermore, the depth of penetration of UV light during treatment is limited because of strong absorption by both catalyst particles and dissolved organic species. Immobilization of TiO_2 on inert surfaces such as glass beads, activated carbon, cotton and cement surfaces can solve this problem, thereby reducing the costs associated with the long settling times or filtration methods for its recovery (Huang *et al.* 2006; Hosseini *et al.* 2007; Yao *et al.* 2010). In addition, immobilization allows superior adsorption properties and increases surface HO• (Lazar *et al.* 2012). A photoreactor combining UV light and TiO_2 immobilized in cellulosic fabric was previously operated for the photocatalytic degradation of model dyes, erythrosine and eosin, leading to high colour removals (Pereira *et al.* 2013). The feasibility of this reactor as a pre-treatment for decolourization and detoxification of dyes as post-treatment for decolourization of biorecalcitrant dyes and dye residues after biological treatment, was previously demonstrated (Harrelkas *et al.* 2008). The aim of the present work was to apply and evaluate the efficiency of the process to real wastewater with very poor biodegradability since most studies deal with model dyes, which are not fully representative of a real process.

EXPERIMENTAL

Textile wastewaters

Two real effluents were collected after the dyeing process from textile companies in the north of Portugal: Valintece SA (ReV) and Gravotextil SA (ReG). Dyeing baths were constituted by three different azo dyes: Remazol Blue RR (RB), Remazol Brilliant Yellow (RBY), Remazol Yellow RR (Y), for ReV, and Imafix Orange (IO), Tecnofix Blue (TB), Tecnofix Red (TR), for ReG. Salts and detergents, softeners, surfactants and sizing, coating and finishing additives were also present. The exact composition of the baths before and after dyeing was not provided. Effluents were characterized in terms of colour, pH, chemical oxygen demand (COD), SO_4^{2-}, NO_3^{2-}, NO_2^- and conductivity. Prior to photo or biological treatments, the real wastewaters were centrifuged at 4,000 rpm for 15 min to remove small pieces of cotton fibre. A model wastewater (MoG) was also prepared by mixing the dyes (provided by Gravotextil) at an equal concentration, 0.1 gL^{-1}. Solutions of single dyes were prepared in deionized water at a final concentration of 0.1 gL^{-1}. Table 1 summarizes the wastewaters and model bath characteristics. The spectra of tested baths are shown in Figure S1 (available online at http://www.iwaponline.com/wst/070/428.pdf).

Biological treatment

Biological assays were conducted in 70 mL serum bottles, each sealed with a butyl rubber stopper, containing 25 mL of either real or model wastewaters and of the single dye solutions. The primary electron donating substrate was composed of 2 gL^{-1} COD of an NaOH-neutralized volatile fatty acids (VFAs) mixture: acetate, propionate and butyrate in a COD-based ratio of 1:10:10. Basal nutrients were (gL^{-1}): NH_4Cl (2.8), $CaCl_2$ (0.06), KH_2PO_4 (2.5), $MgSO_4{\cdot}7H_2O$ (1.0). Non-adapted anaerobic granular sludge was added at a concentration of 2.5 ± 0.5 g L^{-1} volatile suspended solids. Reaction medium was buffered with $NaHCO_3$ (2.5 gL^{-1}) and the headspace flushed with a mixture of N_2/CO_2 (80/20 vol/vol) to the final pH 7.2 ± 0.2. Following the addition of 0.125 mol L^{-1} Na_2S, under strict anaerobic conditions, the flasks were incubated at 37 °C and stirred at 120 rpm. Controls without biomass were also available to control the stability of dyes under experimental conditions.

Table 1 | Wastewaters characterization

Wastewater	Abs at λ_{max}	pH	COD (gL^{-1})	SO_4^{2-} (mgL^{-1})	NO_3^- (mgL^{-1})	NO_2^- (mgL^{-1})	Conductivity (mS)
ReV	0.15 at 420 nm	10.1	9.8	263	3.98	0.020	24.0
ReG	8.0 at 490 nm	10.4	12.0	647	68.2	24.3	45.6
MoG	2.0 at 510 nm	7.0 or 5.5	3.4	nd	nd	nd	nd
IO	1.27 at 470 nm	7.0 or 5.5	3.1	nd	nd	nd	nd
TB	1.27 at 600 nm	7.0 or 5.5	3.2	nd	nd	nd	nd
TR	1.12 at 540 nm	7.0 or 5.5	3.2	nd	nd	nd	nd

nd – not determined.

The effect of wastewater on the methanogenic consortium was performed in similar conditions, but in serum bottles of 25 mL, containing 12.5 mL of the tested solution: ReG and MoG baths, before and after phototreatment. The control contained only VFAs and the blank any substrate. The pressure was measured every 60 min by a hand-held pressure transducer (PSI-30-2 Bar, CentrePoint Electronics Galway, Ireland) capable of measuring a pressure variation of ±202.6 kPa (0 to 202.6 kPa) with a minimum detectable variation of 0.5 kPa, corresponding to 0.05 mL of biogas in a 10 mL headspace. The assay was finished when the pressure remained stable. Methane content of the biogas was measured by gas chromatography as previously described (Pereira *et al.* 2013). For activity determination, the pressure values (calibrated as an analogical signal in mV) were plotted as a function of time and the initial slopes were calculated. Background methane production due to the residual substrate was subtracted (blank). All experiments were performed in triplicate. The effect of tested compounds was evaluated by comparison with the control.

UV/TiO_2 phototreatment

Photodegradation experiments were conducted in a recirculation photocatalytic reactor as described elsewhere (Pereira *et al.* 2013). The photoreactor consists of a 37° slanted aluminum plate with a surface working area of $30 \times 9 \times 30\ cm^2$ (Figure 1). An Erlenmeyer flask containing 300 mL of the effluent to be treated was maintained under agitation during the entire operation and also open to air to ensure sufficient oxygenation. The medium was continuously circulated in the system at a constant flow rate of 200 mL min^{-1}. A thin film flowed from the top of the chamber over a nonwoven fabric made of cellulose fibres on which Tiona PC500 TiO_2 (18 gm^{-2}), UOP 2000 zeolite (2 gm^{-2}) and Snowtex 50 SiO_2 (20 gm^{-2}) were fixed by compression (Ahlstrom, Pont-Evêque, France). The function of zeolite is to increase the hydrophobicity and the adsorbent character of the cellulosic fibre, two important factors for the efficient performance of the catalyst. Artificial irradiation was provided by two UV lamps, positioned in parallel to the reactor, emitting light with a wavelength of around 365 nm (F15T8, BLB 15W; Duke, Essen, Germany). At the end of each assay, cellulose fibre coated with the catalyst was washed and regenerated by circulating deionized water with a few drops of 9% hydrogen peroxide under UV light irradiation (Khataee *et al.* 2009). Triplicate assays using the same fabric were carried out and the error was below 10%. Assays included the effluents ReV, ReG and MoG and single dye IO, TB, TR. solutions. Adsorption measurements of the dyes on immobilized TiO_2 were made using the same setup, in the absence of irradiation. Dye degradation with only UV light in the absence of the fabric containing the TiO_2, was also evaluated.

Analytic assays

Colour decrease was monitored spectrophotometrically in a 96-well plate reader (ELISA BioTek, Izasa, Barcelona, Spain): at selected intervals, samples were withdrawn and diluted in deionized water, to obtain an absorbance below 1. The visible spectra (300–900 nm) were recorded and dye concentration calculated at λ_{max}. First order reduction rate constants were calculated with OriginPro 6.1 software (Northampton, MA, USA), applying the exponential decay curve

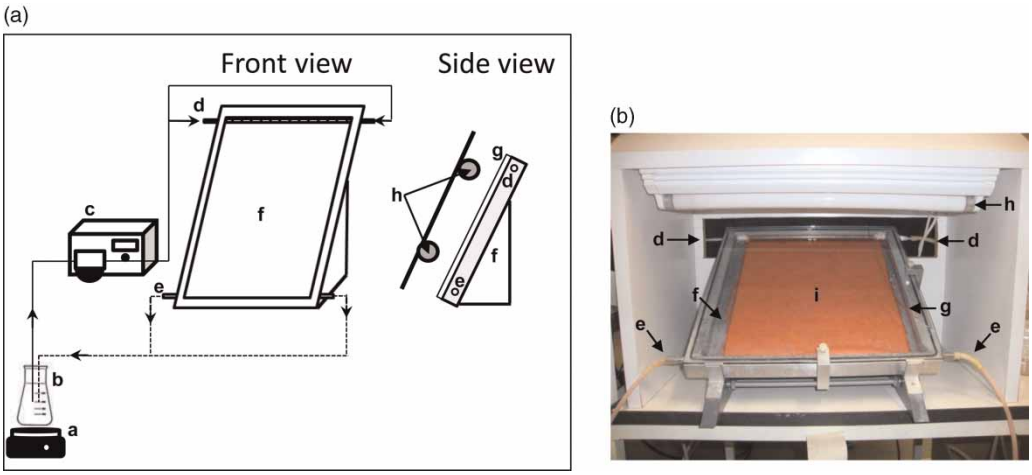

Figure 1 | (a) Schematic diagram of the experimental set-up and (b) photoreactor photography. a, stirring plate; b, reservoir, c, pump; d, feed from pump; e, flow to reservoir; f, catalyst support; g, glass cover; h, lamps; i, catalyst (cellulosic fibre with TiO_2).

represented by the equation $C_t = C_0 + C_i e^{kt}$, where C_t is the concentration at time t, C_0, the offset, C_i, the concentration at initial time and k, the first-order rate constant (d^{-1}). Samples were also analysed by HPLC in a JASCOAS-2057 Plus chromatograph (JASCO, Tokyo, Japan) equipped with a Diode Array Detector. A C18 reverse phase Nucleodur MNC18 column (250 × 9 × 4.0 mm, 5 μM particles and 100 Å pores size; Macherey-Nagel, Oensingen, Switzerland) was used. The mobile phase was 10 mM ammonium acetate (A) and acetonitrile (B). Compounds were eluted at a flow rate of 0.5 mL min^{-1}, room temperature, with isocratic condition at 40% of B over 10 min, followed by a gradient to 80% of B during 10 min and remaining in these conditions for a further 10 min. COD, SO_4^{2-}, NO_3^{2-} , NO_2^- were evaluated with kits from Hach-Lange (Dusseldorf, Germany) at the appropriate range; pH was controlled using a pH meter (HI 83141, HANNA Instruments, Woonsocket, Rhode Island, USA) and conductivity was measured at room temperature using a CRISON conductometer 522 (CRISON Instruments S.A., Barcelona, Spain).

RESULTS AND DISCUSSION

Anaerobic biological treatment

No decolourization was obtained with real wastewaters (Table 2). Conversely, 86% decolourization and 46% COD removal was achieved with the MoG. All three dyes studied were also decolourized to a high extent: 94, 75 and 73%, for IO, TB and TR, respectively (Figure S2; available online at http://www.iwaponline.com/wst/070/428.pdf). However, between them, rates differ significantly, TB was decolourized at a 3-fold higher rate than IO and at a 6-fold higher rate than TR. These differences can be explained by diverse factors such as the molecular structure of the dyes, pKa and potential redox of the dye (Van der Zee & Villaverde 2005). In terms of COD, biological treatment of single dyes led to ~50% removal. The lower initial COD values of single dyes and MoG reveal that the dyes contribute only to a small portion of the COD. The positive decolourization results obtained with single dyes and model baths demonstrate the effect of the other additives present in the effluents, which harm the biological process for the treatment of real effluents.

Table 2 | Decolourization extent (%) and rates (d^{-1}) and COD removal (%), obtained by bio and phototreatment (standard deviations were below 10%)

	Bio-treatment			UV/TiO_2 phototreatment		
	Decolourization			Decolourization		
Wastewater	(%)	(d^{-1})	COD (%)	(%)	(d^{-1})	COD (%)
ReV, original pH	na	Na	na	33	0.5	2
ReV, corrected pH	na	Na	na	42	1.0	5
ReV, controlled pH	0	0	0	69	12.3	29
ReG, original pH	na	Na	na	0	0	0
ReG, corrected pH	na	Na	na	43	2.2	2
ReG, controlled pH	0	0	0	83	3.5	57
MoG, controlled pH	86	5.4	46	87	23.1	78
IO, controlled pH	94	23.1	48	90	14.4	83
TB, controlled pH	75	75.1	50	100	29.9	72
TR, controlled pH	73	2.0	48	88	106.1	55

na – not applicable.

The effect of ReG and MoG wastewaters on the methanogenic consortium was also evaluated. No activity was obtained in the presence of ReG, while with MoG the activity was 93%, as compared with the control (not shown). This finding is in accordance with the decolourization results. Previously, other dyes showed toxicity to the anaerobic microorganisms leading to inhibition of methanogenic activity (Van der Zee *et al.* 2001). However, the high activity obtained with the model bath reveals that the reactive dyes present in the effluent are not toxic and, accordingly, the high alkalinity and other chemicals present in water probably affect the biological process. Some authors have found that sulphate at concentrations up to 60 mM does not inhibit biological azo dye reduction and in some cases, even enhances it (Albuquerque *et al.* 2005; Van der Zee & Villaverde 2005). Conversely, nitrate has been shown to slow down biological decolourization (Wuhrmann *et al.* 1980; Carliell *et al.* 1995, 1998; Lourenço *et al.* 2000). Some reports on the efficient anaerobic biological decolourization of real effluents treated with waters showed much lower COD and conductivity than those measured for ReG and ReV (Sen & Demirer 2003; Kapdan & Alparslan 2005; Melgoza *et al.* 2004). These higher values are explained by the collection of ReG and ReV immediately at the end of the dyeing process.

UV/TiO_2 phototreatment

UV/TiO_2 photodegradation of the real dyed effluents was firstly studied at the original pH. Among the two effluents, only ReV was decolourized, 33%, but COD removal was 2% (Table 1, Figures 2(a) and 2(b)). When the pH was decreased to 5.5, ReV decolourization increased to 42% and at double the rate, but COD removal remained very low, 5%. In addition, ReG, at corrected pH 5.5, was decolourized, 43%, but COD removal was 2%. During the

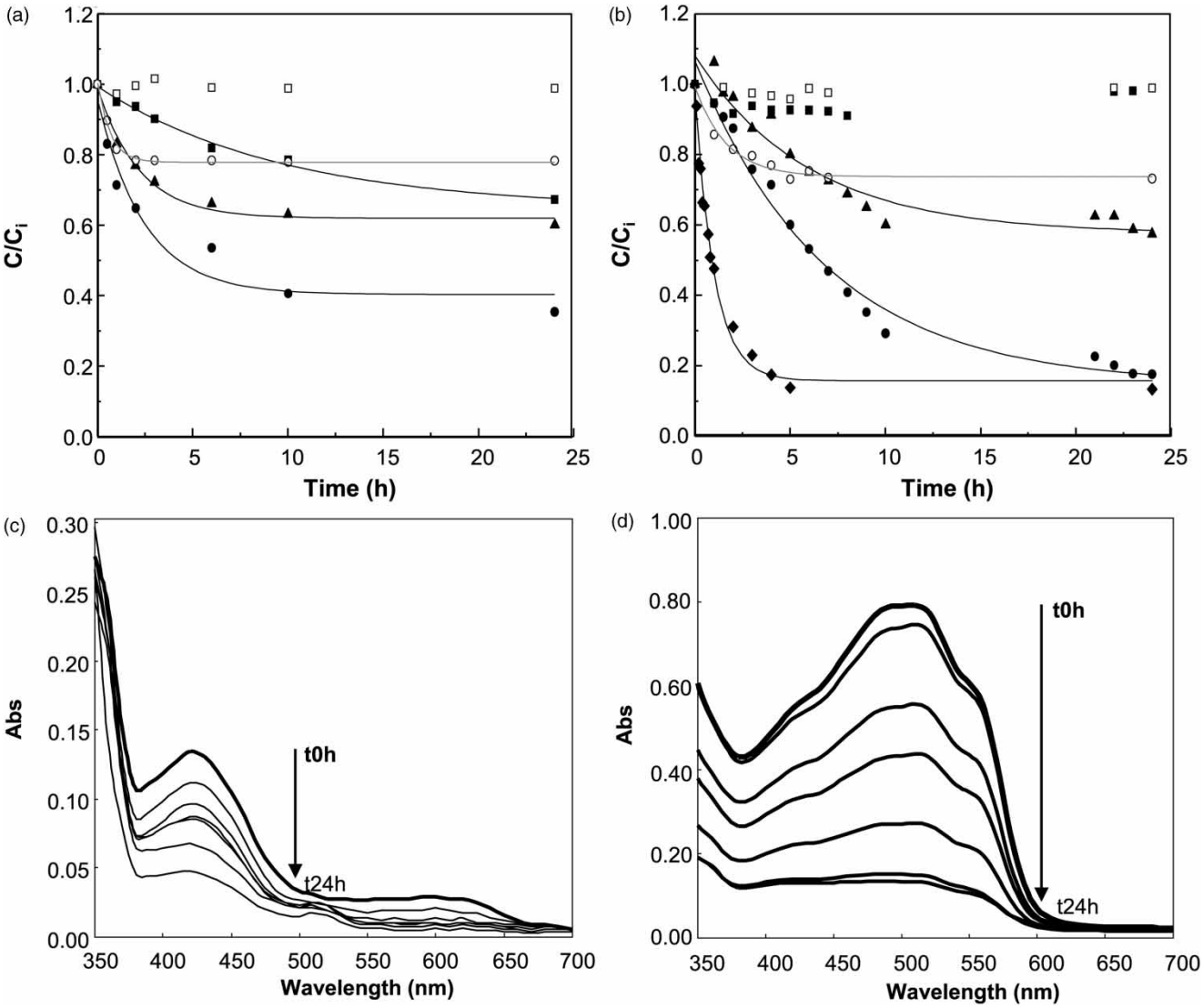

Figure 2 | Photodegradation first-order rate curves at different conditions for ReV (a) and ReG (b) and spectra at controlled pH for ReV (c) and ReG (d). ■, original pH (~10); ▲, corrected pH (5.5); •, controlled pH (5.5); ◆, model bath (pH 5.5). Controls: □, no catalyst and ○, no UV light, at controlled pH 5.5.

photocatalytic treatments, the pH of the solution tended to increase to 8–9, which was supposed to affect the reaction. Indeed, pH control over the entire experiment was essential to increase the extent and rates of decolourization: ReV photodegradation at controlled pH, 5.5, led to 69% colour removal at a 12-fold higher rate as compared with the reaction at not controlled pH, and 29% of COD removal (Figures 2(a) and 2(c)). Interestingly, for ReG the pH control led to almost the double the rate of colour removal, 83%, and to a large COD removal 57% (Figures 2(b) and 2(d)). The effect of pH on the UV/TiO_2 process was already demonstrated for xanthene dyes in our previous report (Pereira *et al.* 2013) and is explained by the effect of the pH of aqueous solution on the charge of dyes and TiO_2. The pH at which the surface of an oxide is uncharged is defined as the zero point charge (pH_{zpc}), being around pH 7 for TiO_2 (Singh *et al.* 2011). In an aqueous environment TiO_2 becomes positively charged below the pH_{pzc}, due to the presence of $TiOH^{2+}$ groups, and negatively charged above the pH_{pzc}, owing to TiO^- groups (Su *et al.* 2009; Ahmed *et al.* 2011). Accordingly, at pH 5.5 it will be negatively charged. Contrarily, the reactive dyes are anionic, thus in solution became negatively charged. Consequently, the electrostatic attractions caused by the opposite charges of anionic dyes and TiO_2 explain the best results at pH 5.5. At higher pH, repulsive forces between the negatively charged catalyst and dye anions hinder the process. So, the adsorption affinity of the dyes on the catalyst surface may be regarded as a critical

step towards efficient photocatalysis, since adsorbed dyes on the surface of TiO_2 will be mineralized by the OH radicals generated by UV light. Indeed, in the absence of light, but with the cellulosic fibre with the catalyst, at controlled pH (5.5), ~22% of decolourization was obtained for the effluent of Valintece and ~27% for the effluent of Gravotextil, occurring only initially (Figures 2(a) and 2(b)). No colour removal or COD removal were obtained for both effluents with the process without the catalyst, meaning that the dyes present are stable in light.

Phototreated water caused no methanogenic activity inhibition, also revealing the efficiency of the process on detoxification (not shown).

MoG was also tested at controlled pH 5.5 and although a similar colour removal was obtained as for ReG, the rate was ~7-fold higher. As compared with biological process, the rate of decolourization by phototreatment was ~4-fold superior, and higher COD removal, 78%, was obtained. The reaction was also monitored by HPLC (Figure S3(a); available online at http://www.iwaponline.com/wst/070/428.pdf). The chromatogram of both baths reveals three peaks with retention time (Rt) at 17, 20 and 22 min corresponding to the dyes IO, TR and TB, respectively. After 24 h of photodegradation, a small amount of the dyes IO and TR still exist in ReG, but not in MoG, which was totally decolourized. Any peaks corresponding to product formation were obtained probably due to the mineralization of dyes. The lower percentage of decolourization obtained by spectrophotometry correlates with the contribution of all the components of the mixture for the colour. High colour and COD removal was also obtained for single dyes, with better results for TB. These results differ from those obtained by biological processes, which led to higher decolourization of IO.

As already mentioned, most of the studies on dye degradation deal with single dyes and model baths, which are not really comparable with real wastewaters. Kanmani & Thanasekaran (2003) have also shown the efficiency of UV/TiO_2 phototreatment of a real textile dyeing rinse wastewater collected at different times of the year. However, while the catalyst could be reused several times, since it was in suspension, its removal from the reaction medium required settling overnight, following by supernatant decanting, which is a time-consuming and troublesome process, especially for application to large volumes. In terms of efficiency, it is difficult to compare it with our process due to low information on effluent characteristics, but in terms of COD their effluent had much lower values (0.096–0.316 g L^{-1}).

CONCLUSIONS

Despite the different characteristics of the tested real textile effluents, none was biodecolourized under anaerobic conditions with granular biomass. Likewise, methanogenic activity was totally inhibited. The high colour removal obtained by biological treatment of model baths reveals the negative effect of salts and other chemicals present in waters. Conversely, efficient colour and COD removal was obtained by UV/TiO_2 phototreatment at controlled pH, 5.5. Phototreated solution showed no methanogenic activity inhibition, revealing the efficiency of the process on detoxification. As TiO_2 is immobilized in the cellulosic fibres, it can be reused, reducing the costs of the process.

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